Kinetics of the Aminolysis of Hydrogenated Tallow by Allylamine and Other Primary Amines in Methanol

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Abstract

Kinetics of the aminolysis of hydrogenated tallow by allylamine in methanol solution under sodium methoxide catalysis was studied at several temperatures (60 to 90C) and catalyst concentrations. Under the experimental conditions the triglycerides were rapidly converted to the mixed methyl esters, which slowly reacted with the amine to produce the mixed amides. At constant catalyst concentration, disappearance of triglyceride was found to be first order in triglyceride and in amine. Because rate was found to be directly proportional to catalyst concentration, the experimental over-all rate was $-d[\text{Triglyceride}]/dt = k_3[\text{Triglyceride}][\text{Amine}][\text{RO}^-]$, and k_3 was 2.022 kg^2 mole^{-2} hr^{-1}. A mechanism proposed by Bunnett and Davis for ester aminolysis involving an ester-amine complex formed in a rapid pre-transition-state equilibrium is consistent with thermodynamic terms which reconcile a large negative entropy of activation (-44.17 cal deg^{-1} equivalent^{-1}) and relatively small energy of activation (11.60 kcal equivalent^{-1}). Relative rate constants at 70C under sodium-methoxide catalysis for the aminolysis of hydrogenated tallow by a variety of structurally different primary amines agreed, in general, with those found by others for the ethylene glycol-catalyzed reaction of methyl acetate with the same amines at 25C. However, monoethanolamine reacted nineteen times faster than predicted, which suggested a mechanism involving initial attack by the alkoxy anion of the ethanolamine in the rate detering step, followed by rapid, base-catalyzed, acyl acyl oxygen-to-nitrogen (O → N) migration. The velocity constants and thermodynamic constants reported enable prediction of the time required for specific yields under a variety of experimental conditions.

Introduction

NUMEROUS KINETIC INVESTIGATIONS have been made to elucidate the mechanism of ester aminolysis (1–10). These investigations have revealed the effect of structure on reactivity (4), have demonstrated the influence of solvents (3,4), including water (2,7–10) on rate, and have shown that the reaction is subject to both acid (2) and base catalysis (1,3, 5–10). Particularly noteworthy has been the strong accelerating influence of alkoxide catalysis (1,3,5,6) in nonaqueous systems. Acceleration of this normally slow reaction by alkoxide catalysis has been used successfully in preparative work (11) even with aromatic amines (12) and was found to be especially useful when volatile amines were reacted with fatty esters at room temperature (13). Alkoxide catalysis has been used extensively by the fat industry, since first introduced by Meade in 1949 (14) to accelerate the conversion of methyl esters and of triglycerides to mono- and diethanolamides in both batch (15–18) and continuous processes (19,20). Although these particular aminolyses are known to be fast, especially at high temperatures (20), their specific velocity constants have not been determined. In fact, no comprehensive study of the rate of conversion of triglycerides to amides in homogeneous solution under the influence of alkoxide catalysts has ever been made, although, under heterogeneous conditions and when excess amine was used, pure methyl stearate was rapidly converted, even at room temperature (13).

The purpose of this investigation was: (1) to determine conditions suitable for preparing mixed N-allylamides directly from hydrogenated tallow by a study of the reaction kinetics in methanol solution under sodium methoxide catalysis; (2) to relate rate quantitatively to both temperature and catalyst concentration in order to permit approximate predictions of rate over a variety of operating conditions; (3) to compare rate coefficients for N-allylamine aminolysis with those found for a variety of other primary amines in order to extend the general utility of the relationships determined for allylamine, and (4) to add, within the limits imposed by the experimental results, to the general knowledge concerning the mechanism of ester aminolysis and the influence of structure on rate.

Allylamine was selected as the primary amine to receive most attention in this investigation partly because of its intermediate position in a scale of primary amine reactivities toward both methyl acetate (21) and methyl stearate (13) and partly because of a recent observation (22,23) that pure N-allyl-stearamide can be converted to hard high-melting waxes by simple treatments with benzoyl peroxide at 90C. The wax application was also the reason for using fully hydrogenated tallow.

Methanol was chosen as the solvent to permit the use of sodium methoxide as catalyst and because both methanol and glycerol accelerate ester aminolysis (3, 24). The rate of the reverse reaction is too slow to seriously affect conversion to amide (5). It was expected that under the conditions selected, the difficultly soluble triglycerides would be rapidly converted to soluble mixed methyl esters (25) before the slower aminolysis reactions occurred. In confirmation, in this investigation the aminolyses of tallow and pure methyl stearate had equal rates under the same experimental conditions. Thus the kinetic constants reported here reflect the rate of attack on mixed methyl esters by selected primary amines, although they are reported in units of the respective triglycerides.

Procedure

Reactions were conducted in 25-ml flasks which were charged with hydrogenated tallow (about 1.2 eq/kg), a slight excess of amine (1.18 moles per equivalent of ester), freshly made 2 N sodium methoxide solution (13), and dry methanol, and then sealed and heated in a constant temperature bath. Reaction

TABLE I

Second-Order Rate Constants and Reaction Concentrations for the Aminolysis of Hydrogenated Tallow in Methanol by Primary Amines

Expt. No.	Amine	Concentration, eq/kg [a]			Reaction temp, C	k_2 kg mole^{-1} hr^{-1} [b,f]	%
		Tallow	Amine	Sodium methoxide			
1	Allylamine	1.215	1.440	0.271	60	0.376	±2.01
2	Allylamine	1.215	1.440	0.271	70	0.514	±5.73
3	Allylamine	1.154 [c]	1.424	0.257	70	0.582 [c]	±4.79
4	Allylamine	1.215 [c]	1.424	0.271	70	0.519	±3.15
5	Allylamine	1.231	1.231	0.271	70	0.544	±3.56
6	Allylamine	1.215	1.440	0.271	80	0.821	±7.87
7	Allylamine	1.215	1.440	0.271	90	1.307	±9.58
8	Allylamine	1.215	1.440	0	70	0.0085	±37.4
9	Allylamine	1.215	1.440	0	70	0.0534 [d]	±9.16
10	Allylamine	1.217	1.443	0.122	70	0.229	±10.4
11	Allylamine	1.213	1.438	0.425	70	0.908	±3.49
12	Allylamine	1.211	1.435	0.605	70	1.120	±6.57
13	Allylamine	1.207	1.431	0.845	70	1.744	±6.73
14	Allylamine	1.202	1.425	1.202	70	3.149	±8.08
15	Allylamine	1.213 [e]	1.438	0.271	70	0.168	±5.83
16	Monoethanolamine	1.215	1.440	0.271	70	19.905	±18.2
17	n-Butylamine	1.215	1.440	0.271	70	1.018	±33.4
18	iso-Butylamine	1.215	1.440	0.271	70	0.450	±9.50
19	Benzylamine	1.215	1.440	0.271	70	0.454	±11.1
20	sec-Butylamine	1.215	1.440	0.271	70	0.023	±28.6
21	tert-Butylamine	1.215	1.440	0.271	70	0.0019	

[a] Methanol concentration, 16.877 mole/kg.
[b] Rate constants, k_2 apply to the triglycerides; in terms of ester function these become ($k_2/3$) kg eq^{-1} hr^{-1}.
[c] Hydrogenated soybean oil used in Experiment 3; both Experiments 3 and 4 carried to >90% disappearance of ester equivalents.
[d] In benzene.
[e] Pure methyl stearate was substituted for tallow.
[f] The slope and intercept of the plot of ln [amine]/[ester] versus time, hr, were determined by the method of least squares. Error in % was determined from the variance at 95% confidence limits. Average error at the intercept for the allylamine experiments was ±5.60%.

TABLE II

Representative Rate Determination in Methanol at 70C [a]

Time, hr	(a−x) eq/kg	(b−x) eq/kg	k_2 kg mole^{-1} hr^{-1}
0	1.215	1.440	
0.5	1.034	1.260	0.718
1.0	0.922	1.147	0.648
2.0	0.757	0.982	0.603
3.0	0.650	0.875	0.570
5.0	0.499	0.725	0.539
7.0	0.404	0.629	0.521
8.0	0.359	0.585	0.527
9.0	0.323	0.548	0.532
10.0	0.290	0.515	0.540
14.0	0.211	0.436	0.530
18.0	0.167	0.392	0.507
24.0	0.108	0.333	0.531
		Average	0.564

[a] Sodium methoxide concentration = 0.271 eq/kg. This is experiment 4 of Table I.

temperatures were between 70 and 90C to insure homogeneous conditions while avoiding high pressure. The flasks were withdrawn at predetermined intervals and chilled to stop the reaction. After hydrolysis to destroy soap and catalyst, the crude reaction product was isolated from a benzene solution by evaporation. To determine ester remaining, aliquots of the crude product were saponified by refluxing with 2 N alcoholic potassium hydroxide for 1 hr. Hydrolysis of N-allylstearamide was found to be negligibly slow under these conditions, like that of other simple amides (26).

Second-order rate constants were determined for each experiment using the relationship (27):

$$\ln B/A = k(B_o - A_o)t + \ln B_o/A_o \qquad [1]$$

where A_o and B_o were the initial concentrations, in equivalents per kilogram, of tallow ester and amine,

respectively, and A and B were their concentrations at time t. A plot of ln B/A as a function of time yielded k ($B_o - A_o$) as the slope and ln B_o/A_o as the intercept. From the slope, the constant k_2 (kg. eq.$^{-1}$ hr.$^{-1}$) was evaluated and converted to units of moles of triglycerides (kg. mole^{-1} hr.$^{-1}$) by multiplication by 3.

Slope and intercept were evaluated by the least squares procedure and per cent error was determined from 95% confidence limits after an analysis of variance. The ester remaining, A, at any time, t, was calculated from ester values.

Experimental Results. The velocity constants determined in this investigation are listed together with experiment numbers in Table I. Typical per cent conversions vs time curves and second-order function vs time curves are shown in Figures 1 and 2, respectively (Experiments 1,2,6,7). Approximate obedience to second-order kinetics was characteristics of all of the experiments listed in Table I even when individual experiments were carried to greater than 90% conversion. This is illustrated in Figure 3 which compares the results found for hydrogenated tallow (Experiment 4) and hydrogenated soybean oil (Experiment 3) toward allylamine. Since in both lines data points on the right side are in an experimentally insensitive region, it is not certain whether the differences in slope and rate constant are significant. When values of k_2 were calculated for each point of an experiment, some drift occurred, as shown in Table II for a typical experiment. The significance of this will be discussed in a later section.

Rate dependence on catalyst concentration is illustrated in Figure 4, where graphs of ln B/A vs time are compared at various catalyst levels. A plot
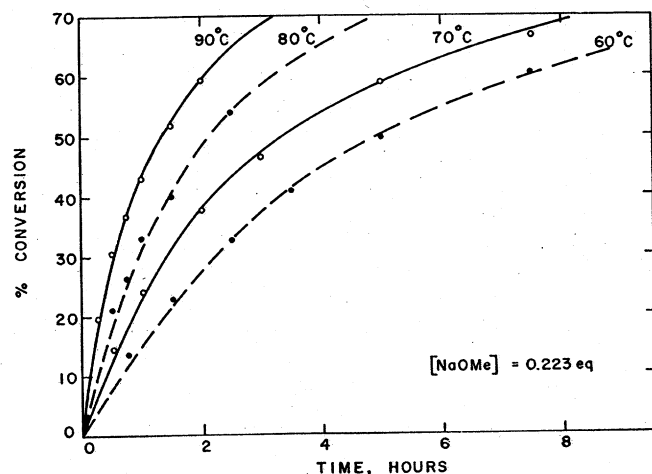

FIG. 1. Plot of per cent conversion vs. time for the aminolysis of tallow by allylamine in methanol at various temperatures, catalyzed by 0.223 eq. of sodium methoxide per ester equivalent.
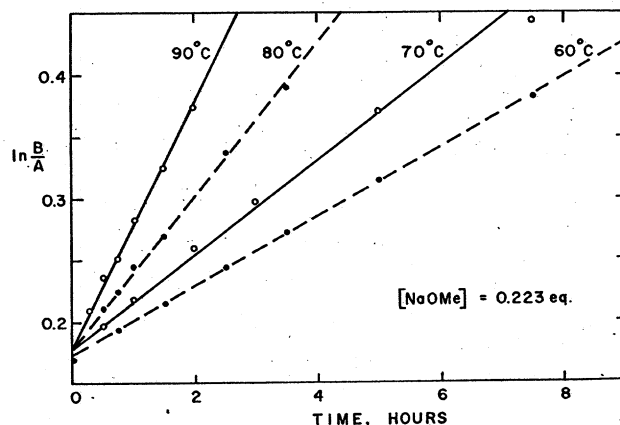

FIG. 2. Second-order plots of the aminolysis of hydrogenated tallow by allylamine in methanol, catalyzed by sodium methoxide, at various temperatures.
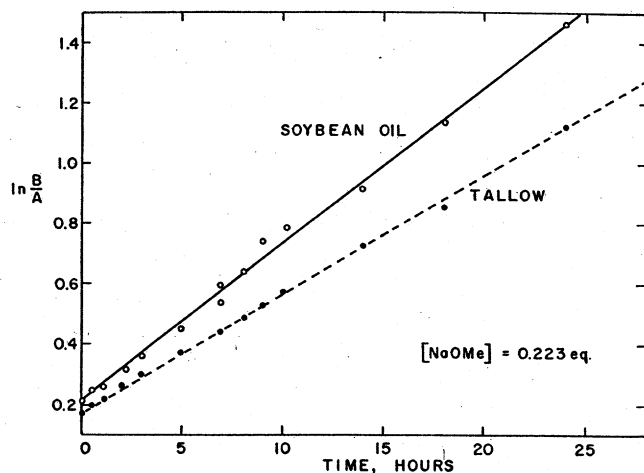
[2]

FIG. 3. Second-order plots of the aminolysis of hydrogenated tallow and soybean oil by allylamine at 70C to greater than 90% conversion.

FIG. 5. Plot of rate constant k_2 vs. catalyst concentration. Evaluation of the third-order rate constant.

of the second-order rate constants derived from these curves (Experiments 1,10–14) as a function of catalyst concentration, shown in Figure 5, established that rate was directly proportional to the concentration of sodium methoxide, as had been previously reported for the reaction of ethyl formate with n-butylamine (6). Therefore the reaction rate was found to be third-order overall, first order in ester; amine, and sodium methoxide respectively, as

$$-d[\text{Triglyceride}]/dt = k_3[\text{Triglyceride}][\text{Amine}][\text{Sodium Methoxide}] \qquad [2]$$

Thus, k_3 is the experimental third-order constant and has the numerical value 2.022 kg^2 mol^{-2} hr^{-1}. Since the intercept of the plot in Figure 5 shows the possibility of a small residual second-order rate for the uncatalyzed reaction, the value of this intercept was determined as a separate experiment (Experiment 8).

Mechanism and Thermodynamics

Of several mechanisms proposed for the aminolysis of esters (1,5–7), the most plausible, especially as it applies to this work is the proposal of Bunnett and Davis (6) for the aminolysis of ethyl formate by n-butylamine in anhydrous solvents. Their mechanism, Equations 3 and 4, calls for an equilibrium between ester and amine rapidly established in a series of steps; reaction of complex I or II with a base B; and finally slow formation of a transition state and loss of alcohol to produce amide:

The disappearance of ester was given by Bunnett and Davis as

Rate $= -d[\text{Ester}]/dt = k_{\text{RO}^-}[\text{Ester}][\text{Amine}][\text{RO}^-] + k_{\text{RNH}_2}[\text{Ester}][\text{Amine}]^2$

$$[5]$$

The first term was thought to dominate in the presence of alkoxide catalysis, which was, of course, used in the present investigation.
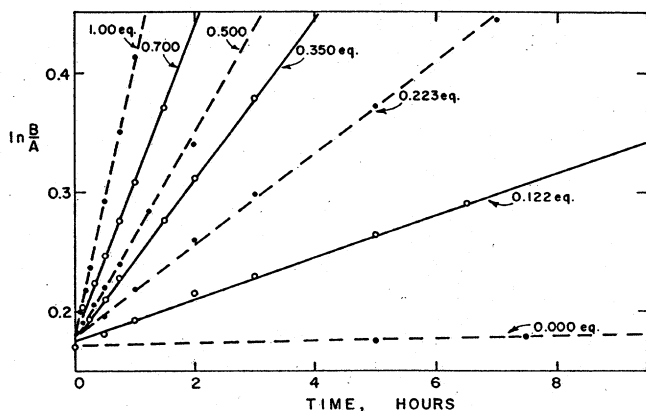

FIG. 4. Effect of sodium methoxide concentration on the aminolysis of hydrogenated tallow at 70C. Sodium methoxide varied from 0 to 1.0 eq. per equivalent of ester.
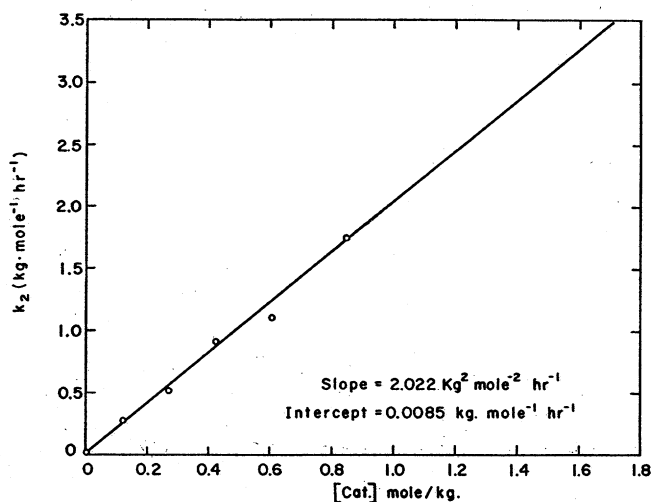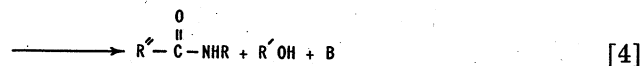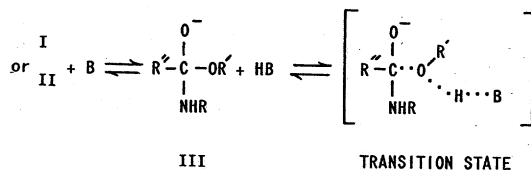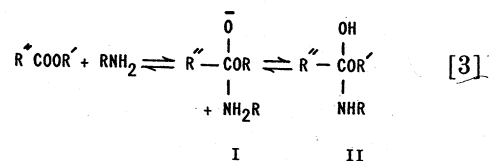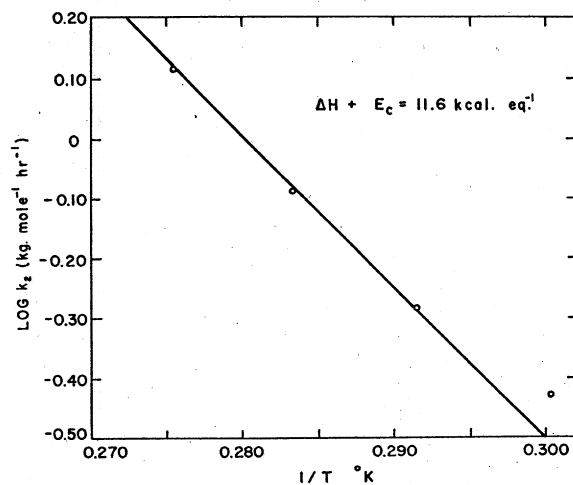

FIG. 6. Determination of energy of activation.

TABLE III
Thermodynamic Constants for the Aminolysis of Hydrogenated Tallow by Allylamine

Constant	Value
$\Delta H + E_c$	11.60 kcal eq⁻¹
log sK₀ [RO⁻]	3.649
RlnK₀ + ΔS*	−44.17 cal deg⁻¹ eq⁻¹ at 70C

TABLE IV
Calculated Reaction Times Required to Convert Hydrogenated Tallow to Mixed Allylamides at Different Temperatures and Amine-Ester Rations[a]

Variation of temperature[b]			Variation of amine/ester ratio[d]		
Reaction temp °C	k₂ (kg mole⁻¹ hr⁻¹ c)	Time, hr, 90% Conv.	Amine/ Ester	Time, hr, 50% Conv.	Time, hr, 90% Conv.
60	0.309	37.9	1.18	3.77	22.8
70	0.514	22.8	1.5	2.76	13.3
80	0.832	14.1	2.0	1.95	7.2
90	1.276	9.2	3.0	1.23	4.7
100	2.021	5.8	4.0	0.89	3.3
125	5.430	2.2	6.0	0.58	2.1
150	13.032	0.90	8.0	0.33	1.5
175	28.447	0.41			
200	57.339	0.20			

a In methanol. Ester concentration 1.215 eq/kg; sodium methoxide, 0.223 eq per ester equivalent.
b At amine/ester ratio of 1.18.
c Calculated using absolute rate expression of Eyring and E_c and ΔS* of Table III.
d At 70C.

Properly speaking, energy and entropy of activation are properties of the transition state. However, equilibria preceding the transition state will contribute to the numerical values of the thermodynamic constants as normally calculated, and it would be more correct in such cases to report the functions in a form that recognizes the equilibria. Appropriate expressions of the functions are developed in the following paragraphs, in which, unless specified, symbols have their conventional significance.

If K is the overall constant for the equilibria leading to II, and k_c is the rate constant for the reaction of alkoxide RO⁻ with a complex consisting of ester E and amine RNH_2, then

$$\text{Rate} = -d[E]/dt = Kk_c([E][RNH_2])[RO^-] \quad [6]$$

In accordance with this scheme, the second-order rate constants of Table I are actually pseudo second-order and are equal to the product Kk_c [RO⁻]. The quantity Kk_c is the slope of the plot given in Figure 5 and is the same as the experimental third-order constant previously mentioned, with the numerical value 2.022 kg² mole⁻² hr⁻¹, for the triglycerides.

Consideration of K as a function of temperature leads to

$$d \ln K/dT = \Delta H/RT^2 \quad [8a]$$

$$\text{or} \quad K = K_o \exp(-\Delta H/RT) \quad [8b]$$

Likewise the relation of k_c to temperature may be expressed (28) by the Eyring equation 9, in which E_c is the activation energy for formation of the transition state from the complex.

$$k_c = \frac{e \, kT}{h} \, e^{\Delta S^*/R} \, e^{-E_c/RT} \quad [9]$$

But, since

$$s = \frac{e \, kT}{h} \, e^{\Delta S^*/R} \quad [10]$$

multiplication of (9) by (8) and substitution of (10) give

$$Kk_c = sK_o e^{-(\Delta H + E_c)/RT} \quad [11]$$

$$\log Kk_c = \frac{-(\Delta H + E_c)}{2.303R} \cdot \frac{1}{T} + \log sK_o \quad [12]$$

$$\log k_2 = \log Kk_c[RO^-] = \frac{-(\Delta H + E_c)}{2.303R} \cdot \frac{1}{T} + \log sK_o[RO^-] \quad [13]$$

It follows that a plot of log k_2 as a function of 1/T should be linear with a slope $-(\Delta H + E_c)/2.303R$ and an intercept log sK_o[RO⁻], in which s is the frequency factor of the Arrhenius Equation (28). Such a plot at 60, 70, 80, and 90C, based on Experiments 1,2,6,7, is shown in Figure 6. The numerical values of $(\Delta H + E_c)$ and log sK_o[RO⁻] were determined by the method of least squares. The 60C experiment was not used in the calculation.

To develop an entropy term recognizing the equilibrium, Equation 10 may be multiplied by K_o giving

$$e(kT/h)K_o \exp(\Delta S^*/R) = sK_o \quad [14]$$

$$\text{or} \quad (R \ln K_o + \Delta S^*) = R(\ln sK_o - \ln kT/h - 1) \quad [15]$$

To calculate the thermodynamic constants, the experimental third-order constant (Kk_c) of 2.022 kg² mole⁻² hr⁻¹ was converted to units of equivalents and seconds, becoming 2.022/3(3600) kg² eq⁻² sec⁻¹. Using equations 13 and 15, overall activation energy, the frequency-factor intercept, and the entropy term were evaluated as in Table III.

The low value of 11.6 kcal found for the activation term above indicates a much higher rate than was actually observed provided that the contribution of ΔH is small. The magnitude of the abnormal negative entropy term −44.1 cal deg⁻¹ eq⁻¹, which greatly exceeds the value of −5 to −8 kcal deg⁻¹ eq⁻¹ usually associated with crowding in the transition state, suggests that pre-transition-state equilibria do occur in aminolysis. Because of the impossibility of separating the terms for equilibrium and rate, no definitive mechanistic conclusion can be reached, however. It is pertinent that the value of R ln $K_o + \Delta S_c^*$ for the uncatalyzed reaction, namely −55.05 cal deg⁻¹ eq⁻¹, is similar to the value of −64 to −67 cal deg⁻¹ eq⁻¹ found by Day and co-workers (29) for the ammonolysis of various methyl esters.

The mechanism discussed in this paper is probably an over-simplification, as has been discussed by Bunnett and Davis (6) and Watanabe and DeFonso (5). The slight drifts found in the constants for individual points (Table II), which are similar to drifts found by others (1,5–7,9,24), suggest that a somewhat more complex situation prevails and that the over-all mechanism might well be a summation of several contributing mechanisms (6). In this work, the best, though not perfect, fit of the data was found by trial to be to the experimental second-order relationship of equation [1].

Calculation of Rate Under Various Conditions

In principle second-order rate constants may be computed for any temperature using the values of $(\Delta H + E_c)$ and log sK_o[RO⁻] given in Table III. Use of the thermodynamic data thus permits the estimation of rate constants at any temperature (up to decomposition) and, therefore, the time required to reach a chosen conversion at that temperature. Table IV lists data computed for several temperatures. Of course, such extrapolated results are only approximate, because of the error involved in the determina-
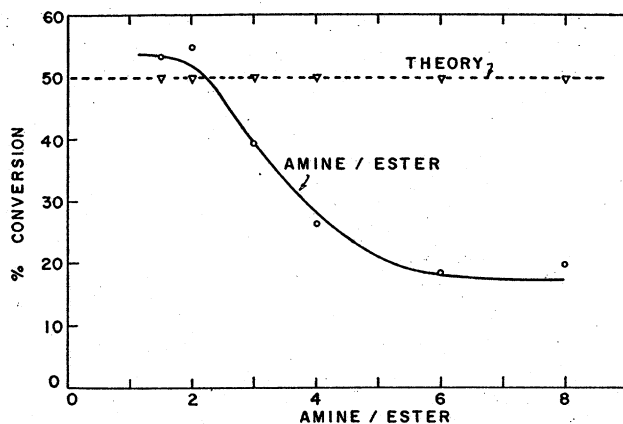
FIG. 7. Effect of variation in the ratio of amine to ester on the per cent conversion of experiments run to calculated half-times.

FIG. 8. Comparative aminolysis of hydrogenated tallow by several primary amines.

tion of activation energy and because the reverse reaction will probably become appreciable at high temperatures.

In a similar way, from the rate constants listed in Table I, the times necessary to reach a desired conversion at increasing amine-to-ester ratios might be estimated by use of an expression of the type below. Thus for a 90% conversion to amide

$$t_{90\%} = [\ln(B/A)_{90\%} - \ln B_o/A_o] \div k_2(B_o - A_o)/3$$

$$[16]$$

In this expression $(B_o - A_o)$ may be varied and has the units assigned earlier. Reaction times calculated for 50 and 90% conversion are also listed in Table IV. To check the range of validity of such extrapolations, a series of experiments, at constant ester and sodium methoxide concentrations and increasing amine concentrations were run for the calculated half-times listed. As can be seen in Figure 7, beyond an amine/ester ratio of 2, the experimental conversions fell well below the calculated curve. Although qualitatively rates were higher at increasing amine/ester ratios, a quantitative proportionality failed as methanol experimentally was progressively replaced by amine. Thus rapid conversion of triglycerides to amide appears to be aided by a large initial ratio of methanol to ester. The decrease in methanol concentration resulting from increase in amine may either have altered relevant activity coefficients or it may have slowed the preliminary conversion of glycerides to methyl esters.

The effect of the use of two different solvents on rate in the absence of added catalyst was studied in the aminolysis of tallow by allylamine at 70C in solution in methanol (Experiment 8) and benzene (Experiment 9). It is assumed that, in the methanol experiment, transesterification precedes aminolysis. The 6.2-fold increase in rate of aminolysis in the benzene experiment is not well understood. Possibly glycerine is a more effective leaving group than methanol. However, solvation effects and competition by methanol could also contribute to the difference.

Relative Rates of Aminolysis

Second-order rate constants for the aminolysis of hydrogenated tallow by a series of primary amines are listed in Table I. Plots of ln B/A vs time, shown in Figure 8, illustrate the large effects on rate caused by structural features of different amines. Such sensitivity to structure indicates again that steric effects contribute to the entropy term, $RlnK_o + \Delta S_c^*$ of Table III. Bulky amines are thought to crowd the
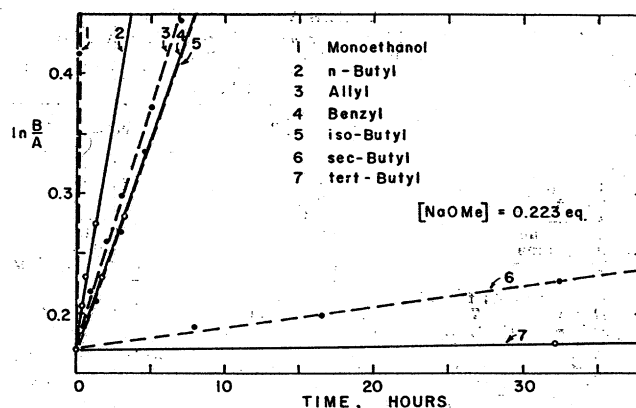
transition state (21), and may also adversely displace a pretransition-state equilibrium. The relative rate constants found in this study at 70C were compared with relative constants determined by Day and coworkers (21) at 25C for the aminolysis of methyl acetate by the same amines in dioxane, catalyzed by ethylene glycol. Values reported in Table V for the isomeric butylamines are in good agreement. The moderate differences in passing to allylamine and benzylamine can be explained by assuming small differences in either energy or entropy of activation (or in both) for these systems. The large difference in the value found for monoethanolamine, however, suggests that, under sodium methoxide catalysis, a change in mechanism occurs.

The acyl moiety of ethanolamides is known to undergo rapid migration from the nitrogen atom to the oxygen atom under strong acid catalysis and from the oxygen atom to nitrogen under basic catalysis (30-32). These shifts, known, respectively, as (N → O) and (O → N) migrations, depend on the pH of the system. In this work it is believed that a rate-determining attack on ester by the alcohol portion of the amine, under the transesterification conditions prevailing, is followed by rapid rearrangement under basic catalysis as shown:

TRANSITION STATE

$$\longrightarrow RC\text{-}NHCH_2CH_2OH + B \qquad\qquad [17]$$
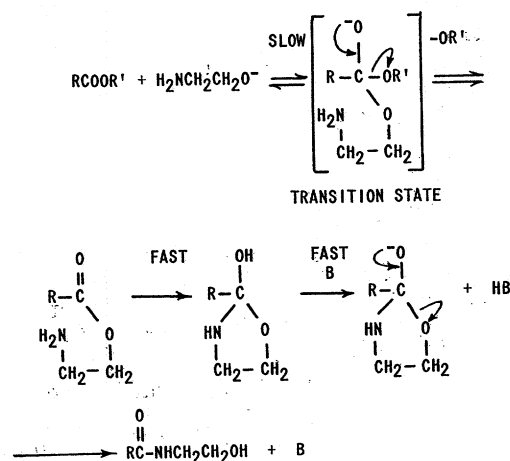
The rate enhancement observed is a reflection of the marked rapidity of transesterification under alkoxide catalysis (25). Additional enhancement can be expected because ethanolamine has been found to be twice as acidic as methanol in isopropyl alcohol solution (33). The value found for the velocity constant using diethanolamine (only approximate because of experimental difficulties) was about one-half the value found using monoethanolamine. Steric and nucleophilic factors, the former very pronounced with